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## Mixed Esters of Brassylic Acid as Plasticizers for Poly (vinylchloride)

**A** previous study on a selected series of brassylic (tri-decanedioic) acid diesters evaluated as plasticizers for poly(vinyl chloride) indicated that several contribute low-temperature properties to the resin comparable to the homologous, commercial adipic, azelaic and sebacic acid diester plasticizers (1). In comparison with these low-temperature plasticizers, brassylate diesters show superior light stability. Brassylic acid, for the preparation of these esters, can be obtained by oxidative ozonolysis

of erucic (*cis*-13-docosenoic) acid. Erucic acid, as glyceride ester, comprises 55-60% of the seed oil of *Crambe abyssinica*, a new oilseed crop being developed under sponsorship of the U.S. Department of Agriculture (2,3). Commercial availability of this oil in the near future is expected to provide an abundant source of erucic acid for industrial utilization.

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Low-temperature plasticizers such as bis(2-ethylhexyl) sebacate (commonly known as "dioctyl sebacate" or DOS) and the brassylates have the same characteristics which could stand improvement; their migration and volatility are poorer than bis(2-ethylhexyl) phthalate (DOP). However one brassylate plasticizer, the dicyclohexyl ester, although somewhat deficient in conferring low-temperature flexibility, has exceptionally low migration and volatility; its physical properties are quite comparable to DOP.

Mixed esters of brassylic acid were prepared in an attempt to improve deficiencies in migration and volatility while retaining good low-temperature flexibility. Alcohol moieties for these mixed esters were chosen on the basis of their properties when combined in diester plasticizers: the cyclohexyl for low migration-volatility loss and the *n*-butyl and 2-ethylhexyl for excellent low-temperature flexibility. The esters were evaluated at levels of 10, 20, 30 and 40% in poly(vinyl chloride).

### Preparation of Esters

The brassylic acid used for esterification was obtained by oxidative ozonolysis of erucic acid. After purification, the brassylic acid was 95-99% pure as determined by gas-liquid chromatography (GLC) (4); detectable impurities were other homologous dibasic acids.

Preparation and purification of the di-*n*-butyl- and dicyclohexyl-brassylate were accomplished as previously reported (1). For the mixed esters, several small-scale trial esterifications were conducted to determine the proper reactant concentrations to give the desired product ratio (25% of each symmetrical diester and 50% of the mixed ester). For the preparation of the mixed 2-ethylhexyl cyclohexyl ester, the reactant ratios finally selected were 1.10 moles of 2-ethylhexanol and 2.74 moles of cyclohexanol per mole of brassylic acid. The 20% Apiezon L. column, employed previously for analyses of the brassylate diesters by GLC (1), did not effectively separate the three component esters in this purified product. Complete separation and analysis were achieved at 230°C with a 1/8-in. x 2-ft. column containing 20% diethylene glycol adipate on 100-150 mesh Celite 545, with a helium flow of 20 ml./min. Area per-

centages were: 24% bis(2-ethylhexyl) brassylate, 28% dicyclohexyl brassylate, and 48% of the mixed 2-ethylhexyl cyclohexyl brassylate. Purification of this ester was accomplished by distillation at 5 $\mu$  Hg in a molecular still. By this procedure the low-boiling contaminants were removed as a forerun and the colored materials were left in the residue.

The mixed *n*-butyl cyclohexyl ester was prepared by reacting 1.05 moles of *n*-butanol and 1.10 moles of cyclohexanol per mole of brassylic acid. After purification, the product was analyzed by GLC. The 20% Apiezon L column was satisfactory in this instance, and the area percentages were 28% di-*n*-butyl brassylate, 20% dicyclohexyl brassylate and 49% of the mixed *n*-butyl cyclohexyl brassylate with 3% of shorter chain-length materials.

The purified products were examined for trace impurities by thin-layer chromatography with Silica Gel G (5) using the previously published procedure (1). The dicyclohexyl ester did not show any impurity by this method, whereas the three remaining ester preparations contained only traces of impurities.

Analytical data on these esters are presented in Table I.

### Evaluation of Brassylates and Controls as PVC Plasticizers

**Formulation**—The four brassylate esters and two commercial plasticizers, used for comparison, were incorporated into a commercial PVC resin (Geon 101) at four different levels of plasticizer content according to the following formulations.

Weight % plasticizer	Parts by weight			
	40	30	20	10
PVC resin (Geon 101)	57	67	77	87
Ba-Cd complex (Mark M)	2	2	2	2
Epoxidized oil (G-60)	1	1	1	1

The plasticizer was added to the dry mixture of stabilizers and resin before milling. Milling was carried out on a 4 x 8 in. rubber mill at 320°F for approximately 8 minutes. The plasticized sheet was then molded in a standard 6 x 6 x 0.075 in. mold. The mold containing the test formulation was first heated to 320°F for 10 minutes without pressure, then pressed at 1000 psi for an additional 10 minutes at 320°F, and cooled under pressure to approximately room temperature.

**Mechanical Testing**—The molded sheets were equilibrated at 73°F and 50% relative humidity for at least 24 hours prior to testing. For the determination of tensile strength, ultimate elongation and 100% modulus, specimens were die-cut from the sheets parallel to the milling axis. Measurements were made on an Instron tester according to ASTM 412-62T (8) at a jaw separation rate of 20 in. per minute for the 20, 30 and 40% plasticized sheets; specimens containing only 10% plasticizer were tested at a jaw separation rate of 0.5 in. per minute. Torsional modulus, as a function of temperature, was determined with a stiffness tester according to ASTM D 1043-61T (8).

**Migration and Volatility**—The procedure of Geenty (9) was used to measure the migration of plasticizer from the resin at 23°C. Volatility was determined at 70°C in Columbia activated carbon, 6 to 14 mesh, in a closed

Table I. Analyses of Brassylate Esters

Ester	Saponification Equivalent <sup>1</sup>		Hydroxyl Value <sup>2</sup> (%)	Acid Value <sup>3</sup>	GLC <sup>4</sup> Purity (area %)
	Calc. <sup>5</sup>	Found			
Di- <i>n</i> -butyl	178	175	Trace	0.04	100
Dicyclohexyl	204	203	0.0	0.31	100
<i>n</i> -Butyl cyclohexyl	202	190	0.0	0.50	— <sup>6</sup>
2-Ethylhexyl cyclohexyl	218	222	0.2	0.30	— <sup>7</sup>

<sup>1</sup> Method of VanEtten (6).

<sup>2</sup> AOCS method Cd 4-40 (7).

<sup>3</sup> AOCS method L3a-57 (7).

<sup>4</sup> Gas-Liquid chromatography.

<sup>5</sup> Calculated from analyses by gas-liquid chromatography.

<sup>6</sup> 28% Di-*n*-butyl, 20% dicyclohexyl, 49% *n*-butyl cyclohexyl brassylate.

<sup>7</sup> 24% Bis(2-ethylhexyl), 28% dicyclohexyl, 48% 2-ethylhexyl cyclohexyl brassylate.

**Table II. Properties of Molded PVC Sheets Containing Brassylate Ester Plasticizers or Controls**

Plasticizer	In Formulation, %	Tensile psi	Tensile Properties <sup>1</sup>		Torsional Stiffness temp., °C		Migration, wt. loss, %	Volatility, wt. loss, %	Heat Stability, hr. to failure (160°C)	Light Stability, (hr./failure)
			100% Modulus psi	Elongation at Break, %	T <sub>135,000</sub>	T <sub>10,000</sub>				
Brassylate:										
Di-n-butyl	40	1690	500	440	—59	—22	32.5	5.7	6.9	648/Exudate
	30	2610	990	360	—52	—14	19.8	2.7	5.9	672/Discolor
	20	3840	2940	160	—16	24	7.8	1.9	4.2	576/Discolor
Dicyclohexyl	10	5800	—	50	40	50	0.2	0.8	2.2	432/Spotting
	40	1930	690	270	—41	—20	14.2	1.0	7.1	816/No failure*
	30	2850	1420	300	—23	5	4.0	0.7	6.4	816/Spotting
	20	3860	3120	140	6	32	0.5	0.6	4.7	816/Spotting + discolor
Mixed n-butyl cyclohexyl	10	6700	—	20	47	55	0.2	0.2	3.8	480/Spotting
	40	1680	490	320	—54	—30	25.4	2.6	7.4	480/Dry exudate
	30	2600	1080	265	—39	0	14.5	2.0	6.5	792/Discolor
	20	3350	2630	180	—5	30	4.3	1.6	5.8	768/Discolor
	10	6010	—	5	41	50	0.03	0.6	4.5	768/Discolor + spotting
Mixed 2-ethylhexyl cyclohexyl	40	1980	660	380	—56	—32	22.8	1.4	5.0	648/Exudate
	30	2760	1310	330	—39	0	10.1	0.9	4.8	504/Discolor
	20	3710	3180	220	—3	36	1.6	0.6	4.7	480/Discolor
	10	6400	—	25	42	52	0.0	0.2	2.1	456/Spotting
Controls:										
Bis(2-ethylhexyl) sebacate (DOS)	40	1860	630	320	—72	—41	30.9	2.7	6.2	96/Exudate
	30	2660	1190	390	—51	—3	17.6	1.4	5.8	168/Exudate
	20	3610	2790	240	—17	31	4.6	0.9	5.7	696/Exudate
	10	5590	—	60	40	51	0.0	0.3	4.1	624/Spotting
Bis(2-ethylhexyl) phthalate (DOP)	40	1990	600	400	—47	—20	12.5	2.7	7.4	552/Exudate
	30	2700	1420	280	—25	7	4.6	2.2	6.9	720/Discolor
	20	3380	2950	190	6	33	0.16	1.6	4.7	720/Discolor
	10	6295	—	30	46	52	0.05	0.6	4.8	312/Spotting

<sup>1</sup> Tensile data at 40, 30, and 20% levels were obtained at 20 in./min.; 10% plasticizer level was run at 0.5 in./min.

<sup>2</sup> Test terminated after 816 hours.

container according to ASTM D 1203-61T, Method A (8). Volatility and migration were studied on approximately 10-mil sheets, which were milled only.

**Heat and Light Stability**—The heat stability of the molded specimens was determined by heating in an air convection oven at 160°C. Samples were removed every 30 minutes and examined for color development in a GE spectrophotometer. The arbitrarily chosen point for failure is when the transmittance of the specimen is less than 20% at 600m $\mu$ .

An Atlas twin-arc Weather-Ometer was used to test the light stability of the molded specimens. During exposure, specimens were subjected to temperatures ranging from 65° to 85°C. Changes in color and physical appearance were noted every 24 hours and evaluated as spotting, discoloration, stiffness, and tacky surface or exudation. The failure of a sample was arbitrarily chosen as the length of exposure required for moderate degradation in any one mode of breakdown or for slight degradation in any three modes of breakdown.

The properties of the plasticized poly(vinyl chloride) sheets are shown in *Table II*.

## Results and Discussion

All the esters tested were compatible with the resin at

levels from 10-40% plasticizer content. The bis(2-ethylhexyl) brassylate was not included in this series because its compatibility with poly(vinyl chloride) was only fair at the 32% level (1). The effect of varying the plasticizer content of the formulation was as expected for both the brassylates and controls. At higher plasticizer levels, tensile strength and 100% modulus are lowered while % elongation is increased. With increased plasticizer content, the low-temperature flexibility and heat stability are improved, but migration and volatility losses are greater.

Earlier comparison of plasticized sheets containing 32% plasticizer indicated that the low-temperature properties imparted by dicyclohexyl brassylate and by commercial DOP are almost identical. Present data indicate that this similarity holds true at all four levels of plasticizer tested. The brassylate ester has excellent heat and light stability with low migration and volatility losses.

Plasticized specimens containing dicyclohexyl brassylate have outstanding properties in comparison with other brassylate diesters, except for low-temperature flexibility. On the other hand, brassylate diesters with excellent low-temperature properties could stand improvement in migration and volatility characteristics. Mixed brassylate esters were therefore prepared in an attempt to improve

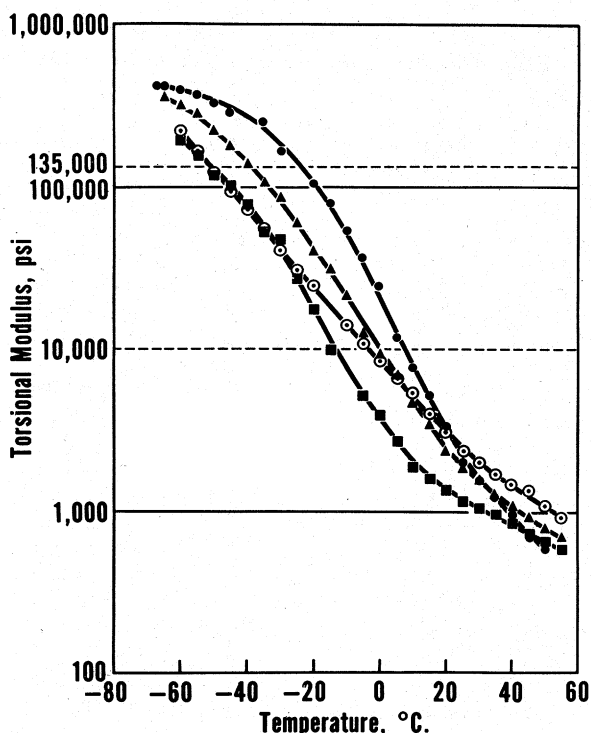


Figure 1. Effect of temperature on flexibility of poly(vinyl chloride) containing 30% of four different plasticizers. Bis(2-ethylhexyl) phthalate (DOP) (—●—●—●—), 2-ethylhexyl cyclohexyl brassylate (—▲—▲—▲—), bis(2-ethylhexyl) sebacate (DOS) (—○—○—○—), and dibutyl brassylate (—■—■—■—).

the low-temperature flexibility of the cyclohexyl moiety while still retaining its other excellent characteristics.

The low-temperature flexibility of plasticized sheets containing the two mixed esters, *n*-butyl cyclohexyl- and 2-ethylhexyl cyclohexyl-brassylate, is just about intermediate between the di-*n*-butyl- and dicyclohexyl-brassylate as might be predicted. Both mixed brassylates confer lower flex temperatures ( $T_{135,000}$ ) and exhibit a slower decrease in flexibility with temperature ( $T_{135,000}$ – $T_{10,000}$ ) than DOP; such a flexibility characteristic is more desirable. Torsional modulus vs. temperature curves are shown in Figure 1 for four of these plasticizers (DOP, the mixed 2-ethylhexyl cyclohexyl ester, dibutyl brassylate, and DOS) incorporated at a level of 30% in the resin. The curve for the mixed butyl cyclohexyl brassylate (not shown) is almost identical to that of the mixed 2-ethylhexyl cyclohexyl ester. Commercial DOS and dibutyl brassylate impart almost identical flex temperatures up to 30% plasticizer; at the 40% level, DOS-plasticized resin remains flexible to a lower temperature (Table II). Specimens plasticized with DOS show a greater difference between  $T_{135,000}$  and  $T_{10,000}$ ; their flexibility is less affected by temperature than those plasticized with the brassylates or DOP.

The migration characteristic of the mixed butyl cyclohexyl ester in the resin is an improvement over the dibutyl, but higher than anticipated. The lower migration of the 2-ethylhexyl cyclohexyl brassylate is somewhat better and more in line with expectation. Both mixed esters show lower migration loss than commercial DOS, but are not as good as either dicyclohexyl brassylate or DOP.

The volatility of the mixed 2-ethylhexyl cyclohexyl brassylate is exceptionally good, approaching that of the dicyclohexyl ester. Both this mixed ester and the dicyclohexyl ester have a volatility lower than either DOS or DOP. Volatility of the mixed butyl cyclohexyl ester in the resin is improved over that of the dibutyl brassylate but less so than expected.

Heat stability of the resin plasticized with the dicyclohexyl ester is somewhat better than that of the dibutyl ester; surprisingly, the mixed butyl cyclohexyl brassylate has better heat stability than either of its parent compounds, and is about the same as commercial DOP. The mixed 2-ethylhexyl cyclohexyl ester was not as good for heat stability as were the other esters tested in this series.

Although there are differences in light stability of the brassylate-plasticized specimens, they are all excellent and are comparable to DOP and superior to DOS. The light stability of DOS is anomalous, being excellent at low plasticizer levels (10–20%) but poor at the higher levels (30–40%) normally used. Also, failure of the DOS was always due to exudation, which is less acceptable than the discoloration or spotting usually noted for the brassylates.

## Summary and Conclusions

Intermediate plasticizer properties are achieved through incorporation of two different alcohol moieties into a brassylic acid ester. A notable exception is the heat stability of the mixed butyl cyclohexyl product, which is better than that of either of its parent compounds. Use of the cyclohexyl moiety as a part of a mixed ester effects a worthwhile lowering of migration and volatility, and plasticized sheets containing 2-ethylhexyl cyclohexyl brassylate have better low-temperature flexibility and lower volatility than those containing DOP. This mixed ester also imparts lower migration-volatility loss and much better light stability to the polymer than DOS. This poly(vinyl chloride) plasticizer should be useful for applications where good low-temperature flexibility, low volatility, and excellent light stability are required.

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## Acknowledgment

The authors are indebted to C. E. McGrew and B. R. Heaton for chemical analyses, to J. W. Hagemann for assistance in preparing esters and performing GLC determinations, and to R. E. Beal for aid in the preparation of brassylic acid.

The Northern and Eastern Laboratories are respective headquarters of the Northern and Eastern Utilization Research and Development Divisions, Agricultural Research Service, U.S. Department of Agriculture. Mention of names of equipment or specific industrial products does not constitute endorsement by the U.S. Department of Agriculture over similar equipment or products not named.

<sup>1</sup> Presented at the Division of Organic Coatings and Plastics Chemistry, 150th national meeting of American Chemical Society, Atlantic City, New Jersey, September 12–17, 1965.